Nanocrystals Show a Quick Route to Change

Cation Exchange is Rapid and Reversible

A research team led by Paul Alivisatos has shown that the process by which one type of cation (positively charged atoms), is exchanged for another, takes place at a much faster rate in nanocrystals than in crystals of extended size, and is fully reversible in nanocrystals; something that is virtually forbidden in micro-sized or bulk crystals under the same environmental conditions. The discovery illustrates another unexpected property of nano-sized systems and could have substantial implications for the burgeoning nanotechnology industry.

The team studied the transformations of nanocrystals of the semiconductor cadmium-selenide (CdSe), for which they have developed synthesis techniques which offer a high degree of control over size and shape (MSD Highlight 03-9). They mixed a solution of CdSe nanocrystals with a small amount of silver nitrate at room temperatures. In less than one second, the silver cations reacted with the CdSe spheres to produce spheres of silver-selenide (Ag_2Se). When these Ag_2Se spheres were mixed with a solution containing an excess amount of cadmium cations, the reaction was reversed. Though the reverse reaction took somewhat longer, about a minute, to complete, the final product was CdSe spheres which were nearly identical in size and shape to the starting material. The Berkeley researchers performed similar tests to transform hollow spheres of cadmium-sulfide into hollow spheres of silver-sulfide, and crystals of cadmium-telluride in the shape of tetrapods into tetrapod crystals of silver-telluride. Again, the transformation reactions were fast, complete, and fully reversible.

The cation exchange reaction offers a versatile route for expanding the range of nanoscale materials with diverse compositions, structures, and shapes without having to develop new synthetic methods to produce each individual nanostructure. It is expected that the cation exchange reaction in the nanocrystals developed here can easily be extended to exchanges with other cations. To date, however, attempts to induce exchanges of anions (negatively charged ions) have not been successful under similar experimental conditions, possibly because the much larger size of the anions, relative to the cations, makes diffusion more difficult. The speed and reversibility of the reactions with the anions demonstrates, however, that inorganic nanocrystals with many of their atoms on the surface are far more chemically dynamic than previously thought and that they behave in chemical reactions more like more like molecules than like extended solids.

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D.H. Son, S.M. Hughes, Y. Yin, A.P. Alivisatos, "Cation Exchange Reactions in Ionic Nanocrystals," *Science* 306, 1009 (2004).